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MANUFACTURING METHOD FOR ETHYLENEDIAMINE-N, N'-DISUCCINIC ACID AND ITS FERRIC COMPLEX SALT

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[There are no amendments to this patent.]

Abstract

Objective

To manufacture the respective isomers and their ferric complex salts in isolated forms from an isomeric mixture of the meso form and the racemic form of ethylenediamine-N,N'-disuccinic acid (abbreviated EDDS below).

Means to solve

To manufacture the meso form and the racemic form of EDDS and the ferric complex salt in isolated forms from a isomer mixture consisting of the meso form and the racemic form of EDDS, which is manufactured through a reaction between maleic anhydride and ethylenediamine, for example, by utilizing the difference in the reaction speed of the meso form and the racemic form of EDDS with triiron tetraoxide in ammonia or an alkali aqueous solution.

Claims

1. Manufacturing method for ethylenediamine-N, N'-disuccinic acid racemic form ferric complex salt, characterized by reacting under heat

(1) an isomeric mixture of the meso form and the racemic form of ethylenediamine-N, N'-disuccinic acid;

(2) triiron tetraoxide in an equimolar amount of the aforementioned racemic form in the Fe conversion;

and (3) ammonia or an alkali metal hydroxide in an equimolar amount of the total sum of the aforementioned meso form and racemic form in an aqueous solution, and separating the ferric complex salt of the aforementioned racemic form as an aqueous solution.

2. Manufacturing method for ethylenediamine-N, N'-disuccinic acid racemic form ferric complex salt, characterized by condensing and/or cooling the aqueous solution of the ferric complex salt of the racemic form, which is separated as an aqueous solution in the aforementioned Claim 1, and obtaining the said ferric complex salt in crystalline form.

3. Manufacturing method for ethylenediamine-N, N'-disuccinic acid meso form ferric complex salt, characterized by reacting under heat

(1) an isomeric mixture of the meso form and the racemic form of ethylenediamine-N, N'-disuccinic acid;

(2) triiron tetraoxide in an equimolar amount of the aforementioned racemic form in the Fe conversion;

and (3) ammonia or an alkali metal hydroxide in an equimolar amount of the total sum of the aforementioned meso form and racemic form in an aqueous solution and separating the ferric complex salt of the aforementioned racemic form as an aqueous solution, then reacting under

heat the obtained insolubles with triiron tetraoxide above an equimolar amount of the meso form in said insolubles through the Fe conversion and ammonia or an alkali metal hydroxide above an equimolar amount in an aqueous solution, and separating the ferric complex salt of the aforementioned meso form as an aqueous solution.

4. Manufacturing method for ethylenediamine-N, N'-disuccinic acid meso form ferric complex salt, characterized by condensing and/or cooling the aqueous solution of the ferric complex salt of the meso form, which is separated as the aqueous solution in the aforementioned Claim 3, and obtaining said ferric complex salt in crystalline form.

5. Manufacturing method for ethylenediamine-N, N'-disuccinic acid, characterized by reacting under heat

(1) an isomeric mixture of the meso form and the racemic form of ethylenediamine-N, N'-disuccinic acid;

(2) triiron tetraoxide in an equimolar amount of the aforementioned racemic form in the Fe conversion;

and (3) ammonia or an alkali metal hydroxide in an equimolar amount of the total sum of the aforementioned meso form and racemic form in an aqueous solution and separating the ferric complex salt of the aforementioned racemic form as an aqueous solution, removing the Fe component as an iron hydroxide by adding an excessive amount of alkali to said aqueous solution, and obtaining the racemic form of ethylenediamine-N, N'-disuccinic acid by converting the filtrate to an acid.

6. Manufacturing method for ethylenediamine-N, N'-disuccinic acid, characterized by reacting under heat

(1) an isomeric mixture of the meso form and the racemic form of ethylenediamine-N, N'-disuccinic acid;

(2) triiron tetraoxide in an equimolar amount of the aforementioned racemic form in the Fe conversion;

and (3) ammonia or an alkali metal hydroxide in an equimolar amount of the total sum of the aforementioned meso form and racemic form in an aqueous solution and filtering the ferric complex salt of the aforementioned racemic form as an aqueous solution, then eluting out solubles by processing insolubles with an aqueous solution of ammonia or an alkali metal hydroxide, and obtaining the meso form of ethylenediamine-N, N'-disuccinic acid by converting the obtained alkaline aqueous solution to an acid.

Detailed explanation of the invention

[0001]

Technical field of the invention

This invention concerns a method for manufacturing the respective isomers and their ferric complex salts in isolated forms from an isomeric mixture of the meso form and the racemic form of ethylenediamine-N, N'-disuccinic acid (abbreviated EDDS below).

[0002]

Prior art

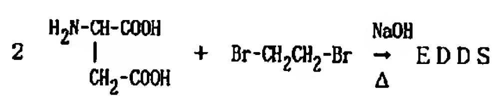
EDDS has been publicly known as a biodegradable compound, and its ferric complex salt also has excellent biodegradable properties. Also, it has been shown that the ferric complex salt of EDDS can be utilized as a photographic processing agent for processing silver halide photographic photosensitive materials that have been exposed (Japanese Kokai Patent Application No. Hei 4[1992]-313752, for example). Furthermore, the descriptions of the manufacturing method for EDDS ferric complex salt can be found in Japanese Kokai Patent Application No. Hei 7[1995]-2745, for example.

[0003]

It is known that the [S,S] form of EDDS can be manufactured using L-aspartic acid and 1,2-dibromoethane as natural materials and through the reaction below, which is also described in Inorganic Chemistry, Vol. 7 (1968), pp. 2405-2412, for example.

[0004]

[Structure 1]



[0005]

However, L-aspartic acid is expensive as an industrial material, and moreover, 1,2-dibromoethane is a compound which is specified as a mutagenic compound with handling dangers in this method, so [this method] is not commonly used in industry.

[0006]

Therefore, as a synthesizing method which uses materials that can be obtained easily and at low cost, a method through which maleic anhydride reacts with ethyleneamine under the presence of alkali, as indicated by the formula below, has been proposed (U.S. Patent No. 3,158,635, for example).

[0007]

[Structure 2]

$$2\ \left.\begin{array}{l}CH-CO\\ \| \\ CH-CO\end{array}\right\rangle O + H_2N-CH_2CH_2-NH_2 \xrightarrow[\Delta]{NaOH} EDDS$$

[0008]

However, in this method, the EDDS that is synthesized is formed as a mixture of a total of 3 kinds of optical isomers, which are [S,S] and [R,R] as the racemic form and [R,S] as the meso form, by the presence of 2 asymmetric carbon atoms, and these must be separated in order to effectively utilize the interaction effect which is peculiar to each isomer. However, a separation method which can be industrially practical has not been established; they [isomers] are only being utilized as an optical isomeric mixture, and the ferric complex salts of said optical isomers are all the same. Also as confirmed by the inventors of this invention, the EDDS racemic form or its ferric complex salt among EDDS or its ferric complex salt particularly has excellent biodegradation properties; it is thought that this characteristic can be further effectively utilized if the EDDS racemic form ferric complex salt can be manufactured in an isolated form.

[0009]

Problems to be solved by the invention

The aim of this invention, which was made while focusing on the aforementioned circumstances, is to offer a method which allows for the manufacture of the meso form and the racemic form of EDDS and its ferric complex salt, which have biodegradation properties and are useful as photographic processing agents, for example, in the respective isolated isomer forms.

[0010]

Means to solve the problems

The essence of the manufacturing method in this invention, in which the aforementioned problem was solved, is reacting under heat (1) an isomeric mixture of the meso form and the racemic form of EDDS; (2) triiron tetraoxide in an equimolar amount of the aforementioned

racemic form in the Fe conversion; and (3) ammonia or an alkali metal hydroxide in an equimolar amount of the total sum of the aforementioned meso form and racemic form in an aqueous solution, and separating the ferric complex salt of the aforementioned racemic form as an aqueous solution, or furthermore, condensing and/or cooling said aqueous solution and obtaining said EDDS racemic form ferric complex salt in crystalline form.

[0011]

Also, the essence of another manufacturing method of this invention is reacting under heat (1) an isomeric mixture of the meso form and the racemic form of EDDS; (2) triiron tetraoxide in an equimolar amount of the aforementioned racemic form in the Fe conversion; and (3) ammonia or alkali metal hydroxide in an equimolar amount of the total sum of the aforementioned meso form and racemic form in an aqueous solution, and separating the ferric complex salt of the aforementioned racemic form as an aqueous solution, then reacting under heat the obtained insolubles with triiron tetraoxide above an equimolar amount of the meso form in said insolubles through the Fe conversion, and ammonia or an alkali metal hydroxide above an equimolar amount in an aqueous solution, separating the ferric complex salt of the aforementioned meso form as an aqueous solution, or furthermore condensing and/or cooling said aqueous solution, and obtaining the EDDS meso form ferric complex salt in crystalline form.

[0012]

Furthermore, the characteristic of the manufacturing method in this invention is reacting under heat (1) an isomeric mixture of the meso form and the racemic form of EDDS; (2) triiron tetraoxide in an equimolar amount of the aforementioned racemic form in the Fe conversion; and (3) ammonia or an alkali metal hydroxide in an equimolar amount of the total sum of the aforementioned meso form and racemic form in an aqueous solution, and separating the ferric complex salt of the aforementioned racemic form as an aqueous solution, eliminating the Fe component as an iron hydroxide by adding an excessive amount of alkali to said aqueous solution, obtaining the racemic form of EDDS by converting the filtrate to an acid, or eluting out solubles by processing solids that remain as insolubles after the aforementioned heat reaction with an aqueous solution of ammonia or an alkali metal hydroxide, and obtaining the meso form of EDDS by converting the obtained alkali aqueous solution to an acidic solution.

[0013]

Embodiment of the invention

As described above, the characteristic of this invention is the manufacture of each isomer and its ferric complex salt in practically isolated forms from a isomer mixture consisting of the meso form and the racemic form of EDDS, which is manufactured through a reaction of maleic anhydride and ethylenediamine, and said characteristic takes advantage of a new property, which has not been confirmed in the past, of the difference in the reaction speed between the meso form and the racemic form of EDDS with triiron tetraoxide in an aqueous solution of ammonia or an alkali metal hydroxide, which allows for the manufacture of the meso form and the racemic form of EDDS and its ferric complex salt in isolated forms through the utilization of said reaction speed.

[0014]

Moreover, as confirmed by the inventors of this invention, as the isomeric mixture, in which the meso form and the racemic form of EDDS coexist, is reacted with triiron tetraoxide in an aqueous solution of ammonia or an alkali metal hydroxide, a ferric complex salt of each isomer is formed, but that formation reaction speed is considerably different between the meso form and the racemic form. Particularly when the amounts of the triiron tetraoxide, ammonia, and alkali hydroxide for EDDS used in the aforementioned processing are properly adjusted, only the racemic form of EDDS forms a ferric complex salt and becomes soluble. Accordingly, as this aqueous solution is separated from the insoluble meso form of EDDS that remains, only the EDDS racemic form ferric complex salt can be obtained in a practically isolated form. Also, as the insolubles that remain are again heat processed in an aqueous solution which includes a proper amount of triiron tetraoxide, ammonia, and an alkali metal hydroxide, the meso form of EDDS contained in said insolubles forms a ferric complex salt and becomes soluble, and the EDDS meso form ferric complex salt can be obtained in a practically isolated form.

[0015]

Also, as an excessive amount of alkali is added to an aqueous solution of the meso form or the racemic form of the EDDS ferric complex salt, which is obtained in the aforementioned manner, the complex salt is dissolved and Fe precipitates as iron hydroxide, and the meso form or the racemic form of EDDS becomes soluble as a 4·alkali salt. As the aqueous solution after eliminating the precipitation of the aforementioned iron hydroxide is changed into an acidic solution by an acid such as hydrochloric acid and sulfuric acid, for example, the meso form or the racemic form precipitates as EDDS·4H, and it becomes possible to obtain the EDDS·4H meso form from the EDDS meso form ferric complex salt or the EDDS·4H racemic form from the

EDDS racemic form ferric complex salt in the respectively isolated forms. This method will be further explained in more detail by separating it as the manufacturing method for the EDDS racemic form or its ferric complex salt and the manufacturing method for the EDDS meso form or its ferric complex salt.

[0016]

First, for the manufacture of the EDDS racemic form ferric complex salt, (1) an isomeric mixture of the meso form and the racemic form of EDDS; (2) triiron tetraoxide in an equimolar amount of the aforementioned racemic form in the Fe conversion; and (3) ammonia (or an alkali metal hydroxide) in an equimolar amount of the total sum of the aforementioned meso form and racemic form are reacted under heat in an aqueous solution. Through this, the racemic form in the aforementioned isomer mixture first reacts with the triiron tetraoxide and ammonia (or alkali metal hydroxide), to form a ferric complex salt, such as [EDDS racemic form]$^{4-}\cdot Fe^{3+}\cdot NH_4^+$, and it becomes soluble in water. Then, a part of the EDDS meso form included in the isomer mixture forms the 1·ammonium salt, but the complex salt is difficult to form, and then remains insoluble; the triiron tetraoxide, which is unreacted and remains, also remains insoluble, and only the EDDS racemic form ferric complex salt can be practically obtained as an aqueous solution when this reaction solution is filtered and the insolubles are eliminated.

[0017]

In the formation reaction of the said EDDS racemic form ferric complex salt, the triiron tetraoxide is used in an equimolar amount in the Fe conversion for the racemic form in the EDDS isomer mixture, and ammonia (or an alkali metal hydroxide) in an equimolar amount is used for the total sum of the meso form and the racemic form, and these are reacted under heat in an aqueous solution. If the amount of the triiron tetraoxide that is used is too excessive, the EDDS meso form also forms a complex salt and becomes soluble; the purity of the obtained EDDS racemic form ferric complex salt becomes low. On the other hand, when it is insufficient, a part of the EDDS racemic form does not form a complex salt and remains as unreacted insolubles, and the yield of the EDDS racemic form ferric complex salt decreases. Also, when ammonia (or alkali metal hydroxide) is used in an excessive amount, a part of the EDDS meso form forms the 2·ammonium salt (or alkali metal salt), becomes soluble, and the purity of the EDDS racemic form ferric complex salt decreases. On the other hand, when it is insufficient, the reactivity of the EDDS meso form also increases because the pH decreases, the aforementioned selective complex salt-forming reaction is inhibited, and the yield of the EDDS racemic form ferric complex salt decreases.

[0018]

Accordingly, for the reaction for the formation of the EDDS racemic form ferric complex salt, it is best to use the triiron tetraoxide in an equimolar amount of the EDDS racemic form in the aforementioned isomer mixture and to use ammonia (or an alkali metal hydroxide) in an equimolar amount of the total sum of the meso form and the racemic form, but this sometimes becomes slightly different from the equimolar amount when used in industry, and about ±10 wt% is acceptable. It is best to perform the aforementioned complex salt-forming reaction within a range of pH 3-7,ideally within a range of pH 4-6. When the pH is too high, the complex salt-forming reaction speed is slow, and a satisfactory yield cannot be obtained. On the other hand, when it is too slow, the selective complex salt-forming reaction of the EDDS racemic form is inhibited, even the meso form forms a complex salt and becomes easily soluble, and the purity of the target substance decreases. The reaction temperature is not particularly limited, but the aforementioned complex salt-forming reaction speed is slow at normal temperature, which requires a long processing time. Also, when it is too high, the complex salt-forming reaction speed is too high, the aforementioned selective complex salt-forming reaction is inhibited, and the purity of the target substance tends to decrease. Therefore, it is preferably within a range of 30-80°C, ideally 50-70°C.

[0019]

The aqueous solution, which is obtained through the elimination of the insolubles in this process, is an aqueous solution which practically contains the EDDS racemic form ferric complex salt and a small amount of ammonia (or an alkali metal hydroxide), and the EDDS racemic form ferric complex salt can be obtained as crystals at a high purity by condensing and/or cooling said solution.

[0020]

When the obtainment of the EDDS·4H racemic form is desired, an excessive amount of alkali is added to the aqueous solution containing the aforementioned EDDS racemic form ferric complex salt, the complex salt is disintegrated, and the Fe component becomes insoluble, is separated, and eliminated as the iron hydroxide, the aqueous solution is converted to an acidic solution with an acid such as hydrochloric acid, sulfuric acid, or nitric acid, for example; then, the EDDS·4H racemic form becomes insoluble and precipitates, and the EDDS·4H racemic form can be obtained through filtration as a highly pure product.

[0021]

On the other hand, in the process for obtaining the aforementioned racemic form ferric complex salt, the insolubles, which are obtained as residuals after the filtration of the aqueous solution including the solubilized EDDS racemic form ferric complex salt, include insolubles that may be mixed as impurities, a small amount of triiron tetraoxide, and the EDDS meso form which has not formed the complex salt, but through the addition of the triiron tetraoxide higher than an equimolar amount in the Fe conversion for the EDDS meso form in said precipitation (insolubles), and ammonia or an alkali metal hydroxide ideally higher than an equimolar amount, ideally over 2 times the molar concentration, and a heat reaction in an aqueous solution, the aforementioned EDDS meso form forms a ferric complex salt and becomes soluble in water, and the ferric complex salt of the EDDS meso form can be obtained as an aqueous solution through filtration from the triiron tetraoxide, for example, which is insoluble and remains, and the EDDS meso form ferric complex salt can be obtained as crystals at a high purity by condensing and/or cooling said solution.

[0022]

At the formation of said EDDS meso form ferric complex salt, the reaction conditions may be set up by mainly considering the complex salt-forming efficiency because the EDDS racemic form is practically not included in the system. A preferable range for the pH is 3-7, ideally 4-6. A preferable range for the temperature is 60-90°C, ideally 70-80°C.

[0023]

Also, when the obtainment of the EDDS·4H meso form is desired, (1) an excessive amount of alkali is added to an aqueous solution which contains the aforementioned EDDS meso form ferric complex salt, the Fe component becomes insoluble, is separated, and eliminated as iron hydroxide through the degradation of the complex salt, the aqueous solution is converted to an acidic solution with an acid such as hydrochloric acid, sulfuric acid, and nitric acid, for example, or (2) for the obtainment of the aforementioned EDDS racemic form ferric complex salt, the insolubles that remain after the separation of the EDDS racemic form ferric complex salt as an aqueous solution are processed with an aqueous solution which contains an excessive amount of ammonia or an alkali metal hydroxide, the EDDS meso form becomes soluble, as the 4·alkali salt, impurities and iron hydroxide, which are insoluble and remain, are separated and eliminated, and the alkaline aqueous solution which is obtained is converted to an acidic solution with an acid such as hydrochloric acid, sulfuric acid, and nitric acid, for example; the EDDS·4H meso form then becomes insoluble and precipitates, and the EDDS·4H meso form can be obtained as a highly pure product through filtration.

[0024]

In this manner in this invention, the meso form and the racemic form of EDDS or their ferric complex salts can be efficiently manufactured as highly pure products from the EDDS isomer mixture, which can be obtained using maleic anhydride and ethylenediamine, for example, as materials through the utilization of the difference in the complex salt-forming reaction speed with the triiron tetraoxide and ammonia (or an alkali metal hydroxide).

[0025]

Application examples

Next, this invention will be explained more concretely with the application examples below; however, this invention should not be limited by the application examples below, and the implementation by properly adding changes within the range of conformity with the essence, which were described previously and will be described later, is included in the technical range of this invention.

[0026]

Application Example 1

200 g EDDS·4H (meso form/racemic form = 45.4/54.6 weight ratio) (purity: 87.0%, meso form: 0.27 mol, and racemic form: 0.33 mol), 40.5 g 25% ammonium hydroxide (0.60 mol), 813 g water, and 25.3 g Fe_3O_4 (0.33 mol as Fe) were placed in a 4-necked 1-liter flask with an agitator and a thermometer attached, reacted at 60°C for 3 h, and the iron in the iron complex salt was oxidized by blowing air into the reaction solution at the same temperature. After the completion of the reaction, the solubles and insolubles were separated through filtration of the reaction solution.

[0027]

The obtained solubles (filtrate) were condensed under reduced pressure until the liquid amount reached 200 g. Crystals precipitated when the temperature of the liquid was cooled to 20°C. These crystals were separated by a centrifuge, washed with a small amount of water and dried at 60°C for 15 h, and 63.4 g of pale-yellow crystal powder was obtained.

[0028]

This crystal powder is the ferric ammonium complex salt of the EDDS racemic form, as clearly indicated in the analytical results below, and the yield for the charged EDDS·4H which can be obtained from the aforementioned yield was 28.4%.

(1)分析結果：				
	EDDS	Fe	NH_4	(2)付着水
(3)含量	76.9%	15.1%	4.5%	3.8%
(4)モル比	1.0	1.0	0.9	0.8

Key:
1 Analytical results
2 Attached water
3 Content
4 Molar ratio

Racemic form purity (liquid chromatograph: refer to Figure 1):
Meso form/racemic form = 0.5%/99.5%, IR spectrum (KBr method): Refer to Figure 2.

[0029]

Application Example 2

In the same manner as the aforementioned Application Example 1, the EDDS·4H meso form/racemic form mixture, ammonium hydroxide, water, and Fe_3O_4 were heat reacted, and a 20% aqueous NaOH solution (1.3 mol NaOH) was added to the solubles, which were obtained through the filtration of the reaction solution after the completion of the reaction; the precipitation which was formed (iron hydroxide) was filtered. A white precipitate was formed when the pH was adjusted to 2.5 by adding hydrochloric acid to the filtrate. This was washed with water and dried, and 61.7 g of a white powder was obtained. For results of the IR analysis and the liquid chromatographic analysis of said white powder, it was confirmed that the EDDS·4H racemic form was 99.5%, the EDDS·4H meso form was 0.5%, and the collection ratio for the EDDS·4H racemic form in the charged EDDS isomer mixture was 65%.

[0030]

Application Example 3

100 g of insolubles filtered in the aforementioned Application Example 1 (unreacted EDDS meso form) (0.34 mol) were placed in a 500-mL 4-necked flask with an agitator and a thermometer attached, 23.1 g 25% ammonium hydroxide (0.34 mol), 400 g water, and 25.5 g Fe_3O_4 (0.34 mol by the Fe conversion) were successively added, then reacted at 80°C for 10 h, and the iron in the iron complex salt was oxidized by blowing air into the reaction solution at 60°C.

[0031]

After completion of the reaction, the insolubles were filtered, and the filtrate was condensed by reducing the pressure until the amount of the reaction solution reached 200 g. Crystals precipitated when the liquid temperature was successively cooled to 20°C; these crystals were separated by a centrifuge, washed with a small amount of water, then dried at 60°C for 15 h, and 66.4 g of a pale-yellow crystalline powder were obtained.

[0032]

This crystalline powder is the ferric ammonium complex salt of the EDDS meso form, as also clearly indicated in the analytical results below, and the yield for the charged EDDS·4H which can be obtained from the aforementioned yield was 53.9%.

(1) 分析結果：

	EDDS	Fe	NH_4	(2) 付着水
(3) 含量	77.6%	15.6%	5.0%	1.8%
(4) モル比	1.0	1.0	1.1	0.4

Key: 1 Analytical results
2 Attached water
3 Content
4 Molar ratio

Meso form purity (liquid chromatograph: refer to Figure 3):
Meso form/racemic form = 92.5%/7.5%, IR spectrum (KBr method): Refer to Figure 4.

[0033]

For reference, Figure 5 shows the liquid chromatograph of the EDDS ferric ammonium, which was obtained by using the [S,S] isomer of the EDDS·4H synthesized using L-aspartic acid and 1,2-dibromoethane as [starting] materials, and Figure 6 shows the IR spectrum (KBr method) of the EDDS·4H which was obtained above.

[0034]

Application Example 4

93.1 g ammonium hydroxide at 25% concentration were added to the insolubles after filtering the solubles in the aforementioned Application Example 1, then dissolved; a white precipitate was formed when the pH was adjusted to 2.5 through the addition of a dilute

hydrochloric acid after filtering the insolubles that remained. This was washed with water and dried, and 54.7 g of a white powder were obtained. As the results of the IR analysis and the liquid chromatographic analysis of said white powder, it was confirmed that the EDDS·4H meso form was 92.5%, the EDDS·4H racemic form was 7.5%, and the collection rate for the EDDS·4H meso form in the charged EDDS isomer mixture was 69%.

[0035]

Comparative example

200 g EDDS·4H (meso form/racemic form = 45.4/54.6 weight ratio) (purity: 87.0%, meso form: 0.27 mol, and racemic form: 0.33 mol), 40.5 g 25% ammonium hydroxide (0.60 mol), 813 g water, and 232 g $FeCl_3$ (0.6 mol as Fe) were placed in a 4-necked 2-liter flask with an agitator and a thermometer attached, reacted at 25°C for 1 h, and this reaction solution was subjected to a liquid chromatographic analysis. Unreacted EDDS was not confirmed; therefore, the pressure of the reaction solution was directly reduced, and [said solution was] condensed until the amount of the reaction solution reached 300 g. A small amount of crystals precipitated during the condensing process, and after the components were checked through filtration [and analysis], ammonium chloride was confirmed. It was further condensed through pressure reduction afterwards, but crystals of the EDDS ferric complex salt were not obtained.

[0036]

Application Example 5

The following experiment was performed to study the effect of temperature and time on the ferric complex salt-forming reactivity of the EDDS·4H meso form and the EDDS·4H racemic form. More precisely, EDDS·4H at a purity of the meso form of 99.8%: 30.0 g (0.10 mol), EDDS·4H at a purity of the racemic form of 99.5%: 30.0 g (0.10 mol); Fe_3O_4: 16.0 g (0.20 mol); 25% ammonium hydroxide: 14.0 g (0.20 mol), and water: 400 g were placed into a 4-necked 500-mL flask with an agitator and a thermometer attached, stirred at the temperatures indicated in Table 1 for the time indicated in said table, and the reaction ratio of the meso form and the racemic form for each temperature and time was checked from the analytical results of the concentration of the EDDS ferric complex salt and the liquid chromatograph of the solution dissolved as the ferric complex salt.

[0037]

Results are as shown in Table 1, the reaction ratio of the meso form and the racemic form was considerably different according to the reaction temperature and the reaction time, but the reaction ratio of the racemic form was higher than that of the meso form in all cases. Also, when

the reaction temperature in particular increases, almost all of the racemic form is reacted, and the reaction ratio of the meso form increases, and as a result, the purity of the racemic form of the ferric complex salt formed through the reaction starts to decrease. Accordingly, the employment of a proper reaction temperature and reaction time is desirable for increasing the purity of the racemic form of the product while assuring a high reaction ratio and selectively reacting the racemic form.

[0038]

Table 1

1 反応温度		2 メソ体・ラセミ体の反応率(%)、括弧内は結晶化後の含有比率				
		0.5時間後 5	1時間後 6	2時間後 7	3時間後 8	4時間後 9
30℃	3 メソ体	0.8 (0.3)	1.6 (0.5)	3.2 (0.5)	4.7 (0.6)	6.2 (0.6)
	4 ラセミ体	17.2 (99.7)	31.4 (99.5)	52.9 (99.5)	67.7 (99.4)	77.9 (99.4)
50℃	3 メソ体	1.5 (0.6)	2.9 (0.8)	5.8 (0.6)	8.6 (0.5)	11.3 (0.9)
	4 ラセミ体	26.6 (99.4)	46.2 (99.2)	71.0 (99.4)	84.4 (99.5)	91.6 (99.1)
60℃	メソ体 3	3.2 (0.3)	6.2 (0.3.)	12.0 (0.5)	17.5 (0.5)	22.6 (--)
	ラセミ体 4	57.1 (99.7)	81.6 (99.7)	96.6 (99.5)	99.4 (99.5)	99.9 (--)
70℃	メソ体 3	10.3 (1.1)	19.5 (--)	35.2 (--)	47.8 (--)	58.0 (--)
	ラセミ体 4	81.8 (98.9)	96.7 (--)	99.9 (--)	99.9 (--)	99.9 (--)
80℃	メソ体 3	16.8 (1.3)	30.8 (--)	52.1 (--)	66.9 (--)	77.1 (--)
	ラセミ体 4	96.8 (98.7)	99.9 (--)	99.9 (--)	99.9 (--)	99.9 (--)
90℃	メソ体 3	26.9 (--)	46.5 (--)	71.4 (--)	84.7 (--)	91.8 (--)
	ラセミ体 4	99.9 (--)	99.9 (--)	99.9 (--)	99.9 (--)	99.9 (--)

10 注：(—) は濃縮・冷却により結晶が析出しなかったものを示している。

Key:
1 Reaction time
2 Reaction ratio (%) of the meso form and the racemic form, the content after crystallization is included within the brackets.
3 Meso form
4 Racemic form
5 After 0.5 h
6 After 1 h
7 After 2 h
8 After 3 h
9 After 4 h
10 Note: (--) indicates those that did not precipitate crystals through condensing and cooling.

[0039]

Through the study of the results in Table 1, the reaction ratio of the racemic form can be sufficiently increased without increasing the reaction ratio of the meso form very much within 0.5 h when the reaction temperature is set to 70°C, about 2 h when the reaction temperature is set to 60°C, about 3-4 h when the reaction temperature is set to 50°C, and over 4 h when the reaction temperature is set to 30°C.

[0040]

Table 1 also includes the purity of the meso form/racemic form of the ferric complex salt of crystals formed through condensing the obtained reaction solutions respectively to 60% and then cooling to 20°C. As clearly shown in these values, the purity of the racemic form of the crystals that are formed through condensing and cooling is significantly higher than the purity of the racemic form of the reaction solution, because it is thought that the racemic form of the ferric complex salt precipitates first when crystallization is obtained from the ferric complex salt of the mixture of the racemic form·meso form. However, when the purity of the racemic form of the reaction solution is lowered to 85%, the meso form in the reaction solution interacts as impurities of the racemic form, and crystals of the ferric complex salt do not precipitate even though the reaction solution is condensed. Then, crystals of the racemic form iron complex salt can be obtained through condensing and cooling if the concentration of the meso form in the reaction solution is up to 15%, and it is understood that the isolation of the racemic form can be sufficiently carried out.

[0041]

Effect of the invention

In this invention as explained above, the meso form and the racemic form of EDDS and their ferric complex salts can be manufactured as individual highly pure products by using the EDDS mixture of optical isomers, which can be obtained by using maleic anhydride and ethylenediamine as materials and by using a simple method. Particularly in this invention, the racemic form, which has a particularly excellent biodegradation property among the aforementioned isomers, and its ferric complex salt can be manufactured in isolated forms, and the characteristics of the EDDS or its ferric complex salt can be further effectively displayed.

Brief description of the figures

Figure 1 is a liquid chromatograph of the EDDS racemic form ferric ammonium salt obtained in Application Example 1.

Figure 2 is an IR spectrum of the EDDS·4H obtained in Application Example 1.

Figure 3 is a liquid chromatograph of the EDDS racemic form ferric ammonium salt obtained in Application Example 2.

Figure 4 is an IR spectrum of the EDDS·4H obtained in Application Example 2.

Figure 5 is a liquid chromatograph of the EDDS ferric ammonium obtained using the [S,S] isomer of EDDS·4H synthesized by the L-aspartic acid and 1,2-dibromoethane.

Figure 6 is an IR spectrum of EDDS·4H synthesized by the L-aspartic acid and 1,2-dibromoethane.

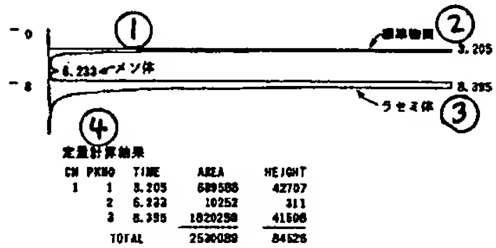


Figure 1

Key:
1 Meso form
2 Standard substance
3 Racemic form
4 Results of the determination calculation

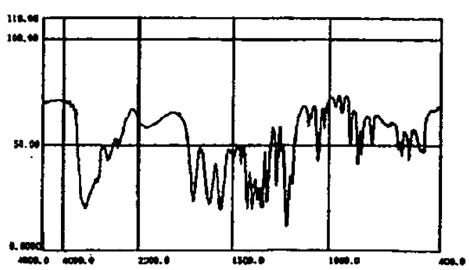


Figure 2

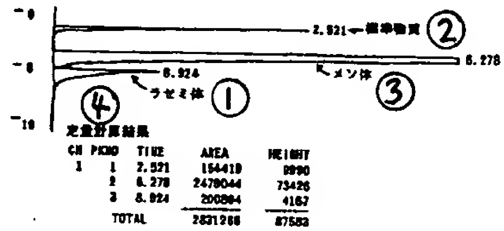


Figure 3

Key:
1 Racemic form
2 Standard substance
3 Meso form
4 Results of the determination calculation

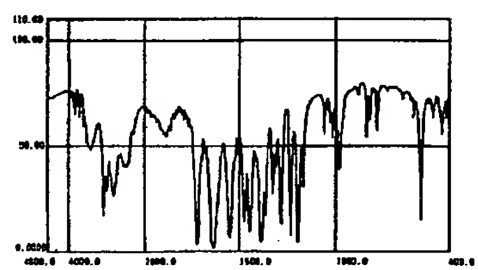
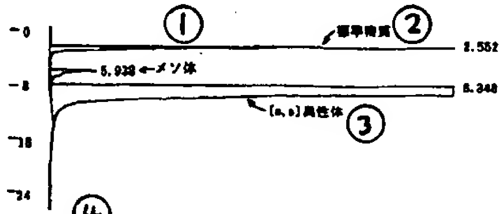


Figure 4



4

定量計算結果

CH	PKNO	TIME	AREA	HEIGHT
1	1	2.552	258785	16343
	2	5.939	50449	1858
	3	8.348	4567183	124442
	TOTAL		4876407	142643

Figure 5

Key:
1 Meso form
2 Standard substance
3 Isomer
4 Results of the determination calculation

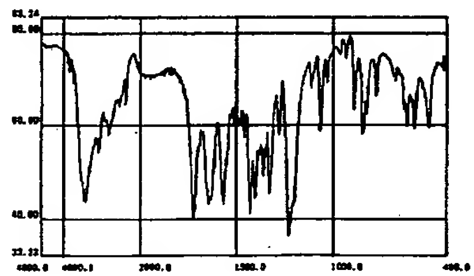


Figure 6